On the Application of Complex Equilibrium Calculations to the Study of
Mineral Matter during Coal Combustion

R. W. Carling, R. W. Mar, and A. S. Nagelberg

Sandia National Laboratories
Livermore, CA 94550

Introduction

Coal is a complex mixture of organic and inorganic materials. The
inorganic portion, the mineral matter, usually makes up a significant
portion of a coal's composition. The contents vary from seam-to-seam but
can be as high as 32 weight percent, with an average of 15 weight
percent for North American coals. Mineral matter acts as a diluent and
is clearly undesirable in mining and transportation. It is also the cause
of many problems within a combustor, such as gaseous and particulate
emissions, fouling, slagging, corrosion, and erosion. With the increased
usage of coal to fulfill the nation's and the world's energy
requirements, higher mineral content coals will play a more significant
role in the future. Therefore, it has become important to understand
the behavior of the mineral matter and its consequences in coal
utilization systems.

In this report we discuss the application of complex thermochemical
calculations to the study of mineral matter behavior during the
combustion of pulverized coal. In principle, one can specify the
conditions of combustion (e.g., temperature, total pressure, and oxygen
partial pressure) and then calculate the chemical equilibrium between
reactions involving all or selected fractions of the elements found in a
coal particle. These calculations may be used to predict the ash and
gaseous species formed during combustion. Practical problems such as
submicron fly ash formation, deposit formation, fouling, and corrosion
may be addressed in this manner. An understanding of the formation of
chemical species and the effects of changes in operating parameters and
system chemistry on stability ranges should aid in identifying control
strategies to combat harmful species. Basically, one is seeking to
improve and control the thermochemical environment of the coal particle
by the proper selection of operating parameters conditions and chemical
constituents.

At the outset, one might question the application of equilibrium
calculations to a nonequilibrium process such as coal combustion. There
might not be time for chemical equilibrium to be attained, and this is
particularly true where the reactants are large particulates.
Equilibrium calculations should be considered an important first step,
to be followed by an examination and incorporation of kinetic aspects.
That is, educated guesses must be made concerning the reactivity and
release of chemical constituents of the coal. Kinetic factors may be

introduced by specifying the chemical state of the calculation, which may differ considerably from the total coal chemistry. Even if equilibrium conditions existed, uncertainties and variations in the calculated results may be introduced by a number of factors. In this paper we address the impact of three potential sources of error on mineral matter calculations, namely: 1) errors in the data, 2) selection of species, and 3) solution formation.

COMPLEX EQUILIBRIUM CALCULATIONS

Numerous methods have been reported for computing complex thermodynamic equilibria, but all methods are based on the methods of Brinkley(1-2) or White, Johnson, and Dantzig(3). Brinkley's approach requires a formulation of independent chemical reactions and the simultaneous solution of equilibrium constant expressions. A superior approach, first suggested by White et al.(3), involves the computation of the composition that minimizes the Gibbs free energy of the system.

A number of independent computer programs to calculate complex equilibria by free energy minimization have been developed over the years(4-7). A major step forward was taken by Erickson(8-10) in his development of codes called SOLGAS and SOLGASMIX. These codes are capable of handling systems containing multiple condensed phases, ideal and nonideal solutions, and mixtures at constant total pressure and temperature. Bessman(11) modified SOLGASMIX to handle the additional case of equilibria at constant gas volume and variable pressure; his version is called SOLGASMIX-PV. Kee and Nagelberg(12) have taken SOLGASMIX-PV and interfaced it with CHEMKIN(13) that allows users at Sandia National Laboratories to share the vast thermochemical data base already available at Sandia.

While the equilibrium state of a complex chemical system is unique, there is no guarantee that all free energy minimization codes will provide the same answer. The Gibbs free energy surface may in fact consist of a number of local minima; thus, a free energy minimization routine could isolate on a local minimum rather than the grand minimum. Different numerical algorithms and convergence criteria selected for the iterative methods of free energy minimization and different programming structures may also lead to conflicting results. For example, Minkoff, Land, and Blander(14) have shown the NASA CEC code(4) to be incapable of converging on a solution when minor amounts of condensed phases are present in delicate balance. By using a primal geometric programming approach, Minkoff et al.(14) were able to eliminate convergence problems. Another cause of inaccurate results, perhaps the most obvious, is erroneous thermochemical data or poor data representation (curve fitting of the data).

A semianthracite coal composition obtained from the Penn State Coal Data Base (PSOC #627) was used in this study. The chemical composition of the coal is shown in Table I. A calculation was carried out in which

this coal was reacted with 20 percent excess oxygen at a pressure of one atmosphere over a temperature range of 1000 to 2000 K. The species considered in the calculation are given in Table II. Thermochemical data for these species were taken from JANAF(15). The sodium-containing species predicted to form in the gas phase during combustion are shown in Figure 1. The major species were NaCl, NaOH, and Na, with NaOH dominating at high temperatures. Na_2SO_4 is predicted to form in lesser concentrations with a maximum peak at 1400 K. The condensed phases predicted to be present are shown in Figure 2. The principle condensed-phase species formed was SiO_2 at all temperatures. Below 1400 K, 2 mole percent Na_2SO_4 was observed as the only other phase. Above 1400 K, the sulfate was replaced by sodium silicate $(Na_2Si_2O_5)$.

The purpose of the calculations described above is not to identify ash formation and deposit formation mechanisms; rather, we will use the results in Figures 1 and 2 as a baseline from which we will illustrate the effects of errors in the data, the number of species considered in the calculation, and solution effects.

EFFECTS OF VARIOUS CALCULATIONAL FACTORS

Errors in the Thermochemical Data

The quality of the thermochemical data used in calculations are often not evaluated when computational codes are used. Durie, Milne, and Smith(16) in their study of salt deposition from hydrocarbon flames, showed a change of only a few kcal/mol in the free energy of formation of a species resulted in a significant rearrangement in the relative proportions of deposited phases. However, one cannot generalize Durie's observations because the effect of a change in the free energy will vary from situation to situation, depending upon the number of chemical constituents, their thermodynamic stabilities, and their relative concentrations.

To illustrate the effect of errors in the data on coal combustion calculations, let us examine the sensitivity of the results to the free energy of Na_2SO_4. Figure 3 shows the predicted distribution of the sodium containing species in the gas phase if the free energy of Na_2SO_4 is reduced by 1 percent (1.2 kcal). It is seen that all curves exhibit the same qualitative behavior as those on Figure 1. In fact, except for the Na_2SO_4 curve, all species were virtually unaffected by the free energy change. The absolute amount of Na_2SO_4 is, of course, reduced.

The magnitude of the change is better illustrated in Figure 4, where the effect of varying the free energy by 1 and 5 percent is shown. In this illustration the situation appears to be buffered, and a drastic rearrangement of the relative proportions of all species does not result if the stability of just one species is modified. However, if one is

(15). Data for the rest of the minerals were taken from the
work of Robie, Hemingway, Schafer, and Haas(17). The calculated gas
phase composition is given in Figure 5, to be compared with that shown
in Figure 1. It is seen that there is a major rearrangement of species,
and as a whole, the species concentrations were all reduced by one to
two orders of magnitude. Major changes also occured with the condensed
phases, as seen in Figure 6. While SiO_2 remained as the primary
condensed phase, Na_2SO_4 and $Na_2Si_2O_5$ were not stable. At temperatures
between 1000 and 1220 K, the stable-condensed phases were SiO_2,
pyrophyllite, and albite. At temperatures greater than 1220 K, the
stable-condensed phases were silica, albite, and mullite. Thus, the results of
complex equilibrium calculations can be significantly altered by the choice of
species. Caution must be used when making the selection, and kinetic factors
and exerimental information should be carefully evaluated.

Condensed Phase Solutions

Previous calculations pertaining to coal combustion have not allowed for
the formation of condensed phase solutions. Solutions will obviously
form when liquid silica, alkali silicates, and sulfates are present.
The results on Figure 2 show that silica and sodium disilicate form, and
the phase diagram information in the literature clearly suggest a
solution will result(18). Let us now extend the baseline calculations
on Figures 1 and 2 to include solution formation. For lack of better
information, we will assume ideal solution behavior. The
sodium-containing gas species formed in this case are shown in Figure 7.
It is seen that the NaCl concentration is not affected, but noticeable
changes in the behavior of NaOH, Na, and Na_2SO_4 is seen. While
their concentrations maintain the same qualitative behavior, they all
form in lesser amounts. Another way of representing the effects of
solution formation is seen in Figure 8, where the ratio of
concentration without solution formation to that where no solution is
formed is shown.

SUMMARY

Complex equilibrium calculations may be a very useful tool in the study
of mineral matter evolution in a coal combustor. Kinetic constraints
must be applied but may be done within the context of equilibrium
calculatons; kinetic considerations may be used to define a more
realistic chemistry for the system. Equilibrium calculations are only
an approximate representation of the real situation since not all
possible chemical species can be considered in a calculation and the
thermodynamic data for many species are uncertain. In order to utilize
the results of complex calculations, one must understand the caveats and
uncertainties created by these problems.

It has been shown that the qualitative behavior of chemical species is
fairly insensitive to errors in the thermochemical data. However, the absolute
concentrations of the species can change by orders of magnitude if the free

concerned with absolute concentrations, great care must be taken to use accurate thermochemical data. A relatively small error of 1 kcal will change the concentration by a factor of two, and a change of two orders of magnitude is realized if a 5 kcal error in assumed. If the interest is in observing changes that occur as parameters are varied (i.e., the movement of phase boundaries), there is a smaller sensitivity to errors in the data.

Errors in data can also result from the misrepresentation of the data in the computer programs. Codes are generally constructed to be of generic use, and thus, a generalized approach to representing the data is used. For example, the NASA CEC code(4) and the Sandia code(12) use multiple-order polynomial fits over two-temperature ranges to represent the data. When dealing with complex condensed-phase mixtures, the free energies must be equal at transition temperatures. Failure to consider this constraint will result in an obvious error, such as a phase predicted to be present under conditions clearly out of its stability range (e.g., a solid phase predicted at temperatures above the melting point).

Species Considered in the Calculation

Complex equilibrium calculations are usually conducted with only a few species for several reasons. First and foremost, there are not many accurate self-consistent data. Also, calculations can become very time consuming, and the possibility of poor convergence behavior increases with the number of species, especially if many species are present in minor amounts(14).

When applying equilibrium calculations to the study of mineral matter behavior, one selects only a few species to consider by making assumptions concerning the reactive chemistry of the system. For example, aluminum is often found in coal but is usually not considered in the calculations because it is assumed to be present in kinetically and thermodynamically inert forms, such as alumino-silicates. If, however, Al is considered in the calculation, a significant change in the calculated results could occur.

To illustrate the point, let us repeat the equilibrium calculations of Figures 1 and 2, this time allowing the following aluminum-containing species to form:

> gas phase: Al, AlO, Al_2O, $AlOH$, Al_2Cl_6
>
> solid phase: Al_2O_3, $Al_6Si_2O_3$(mullite), $NaAlO_2$, $Al_2Si_2O_9H_4$(kaolinite), $NaAlSi_2O_6$(jaedite), $Al_2Si_4O_{12}H_2$(pyrophyllite), Al_2SiO_5(kyanite), $NaAlSi_3O_8$(albite)

For our calculations, the thermochemical data for Al, AlO, Al_2O, $AlOH$, Al_2Cl_6, Al_2O_3, mullite, and $NaAlO_2$ were taken from JANAF

energy of formation is varied by just a few percent. Failure to account for
the formation of condensed phase solutions will also change the absolute
concentrations substantially; however, the qualitative behavior is not
affected as much. The qualitative and quantitative behavior
of product species can be strongly influenced by the selection of species
to be considered in the calculation.

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TABLE I
Chemical analysis of Pennsylvania #2 seam semianthracite coal
(PSOC #627, provided by Pennsylvania State coal data base)

Elemental Analysis (dry)		Analysis of HTA dry coal	
77.08%	carbon	68.50%	SiO_2
2.61	hydrogen	22.80	Al_2O_3
.73	nitrogen	2.93	TiO_2
.52	organic sulfur	2.55	Fe_2O_3
.39	oxygen	.31	MgO
.01	chlorine	.33	CaO
18.67	mineral matter	.16	Na_2O
		1.66	K_2O
		.06	P_2O_5
		.25	SO_3

TABLE II
Chemical Species Considered in Complex Equilibrium Calculations

Gaseous	CO	CO_2	Cl	Cl_2	ClO	H	H_2	H_2O	HCl	H_2S
Species	Na	Na_2	$NaCl$	Na_2Cl_2	NaH	$NaOH$	Na_2SO_4		
	O	O_2	OH	S	S_2	SO	SO_2	SO_3	SiO	SiO_2	SiS

Condensed	C	$NaCl$	$NaOH$	Na_2O	Na_2S
Species	Na_2SO_4	Na_2SiO_3	$Na_2Si_2O_5$	SiO_2	SiC	Si

Figure 2. Condensed phases predicted to form upon the combustion of semianthracite Pennsylvania Seam #2 coal (PSOC #627) in 20% excess oxygen at various combustion temperatures.
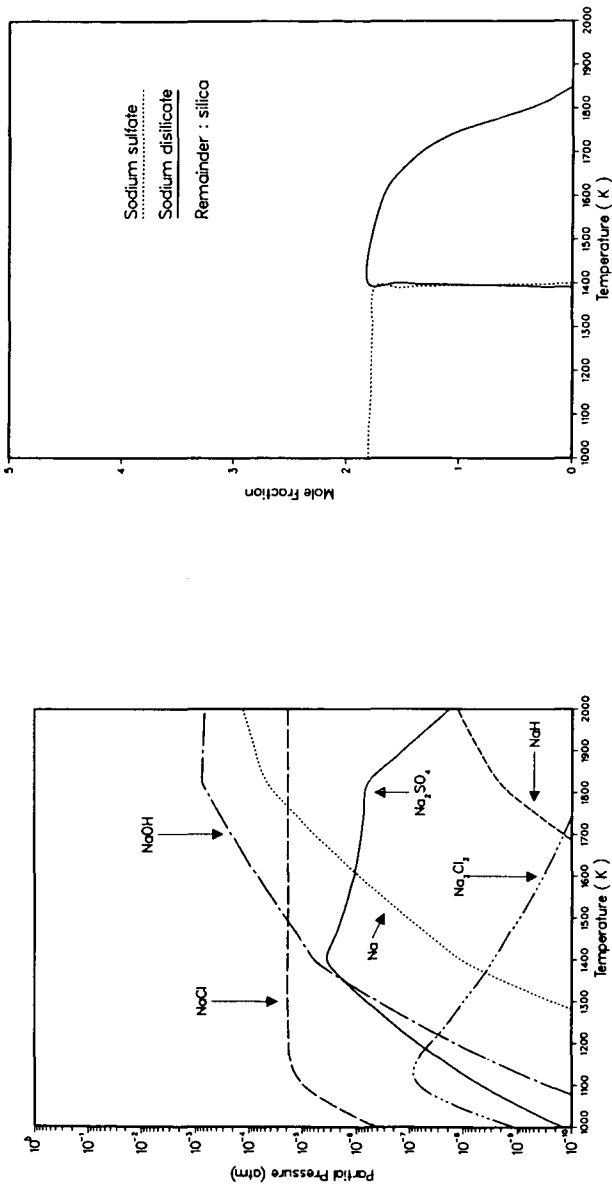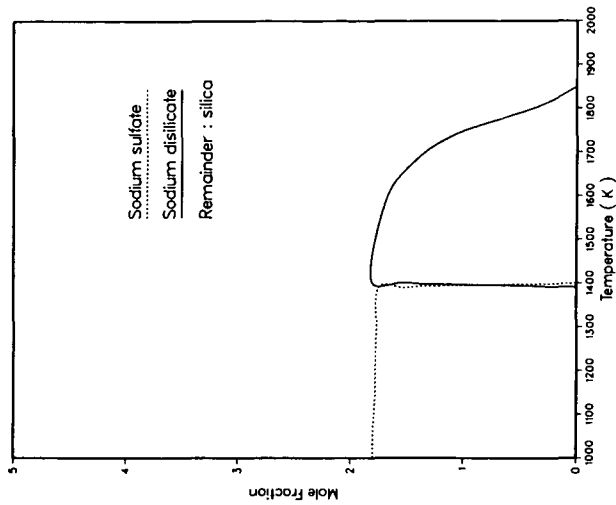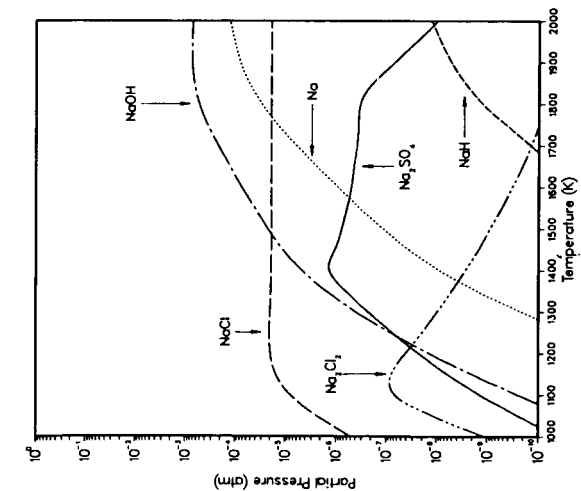

Figure 1. Sodium containing gas species predicted to form upon combustion of semianthracite Pennsylvania Seam #2 coal (PSOC #627) in 20% excess oxygen at various combustion temperatures. Chemical species considered in the calculation are given in Table I.

Figure 4. The effect of varying the free energy of Na_2SO_4; solid line - JANAF data, dotted line - less stable by 1 percent, dashed line - less stable by 5 percent.
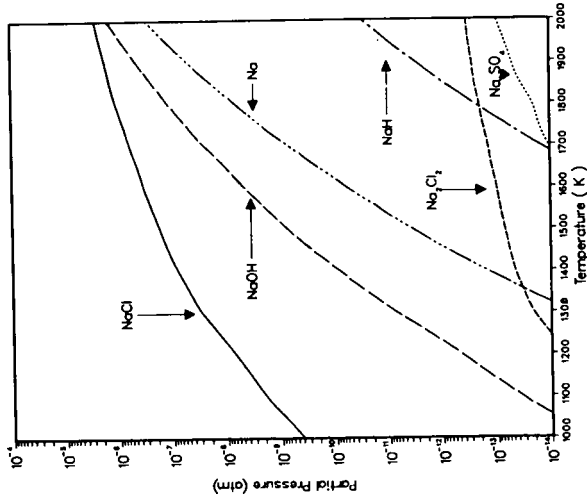

Figure 3. The effect of reducing the free energy of Na_2SO_4 by 1 percent. This distribution of gas species is to be compared with Figure 1.
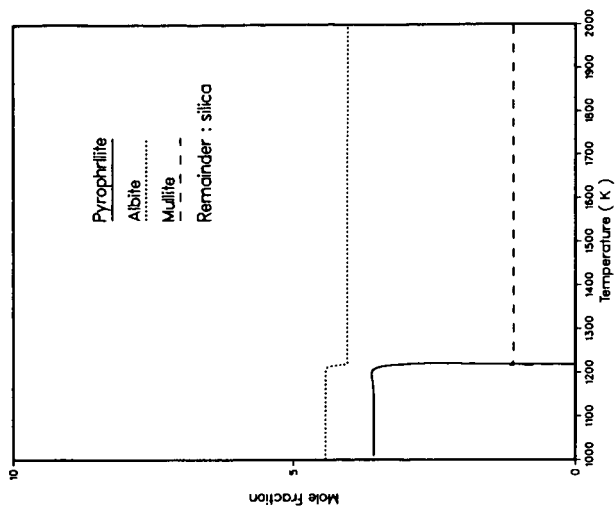
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Figure 6. The effect of considering aluminum containing species in the calculations on the condensed phase distribution. This figure is to be contrasted with Figure 2.
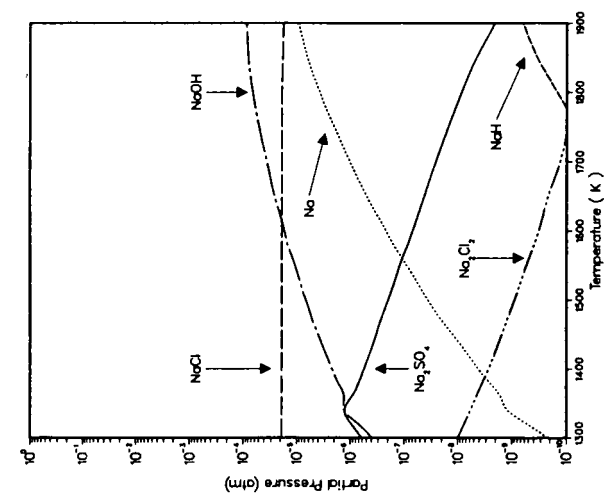

Figure 5. The effect of considering aluminum containing species in the calculations. This distribution is to be compared with that shown on Figure 1.
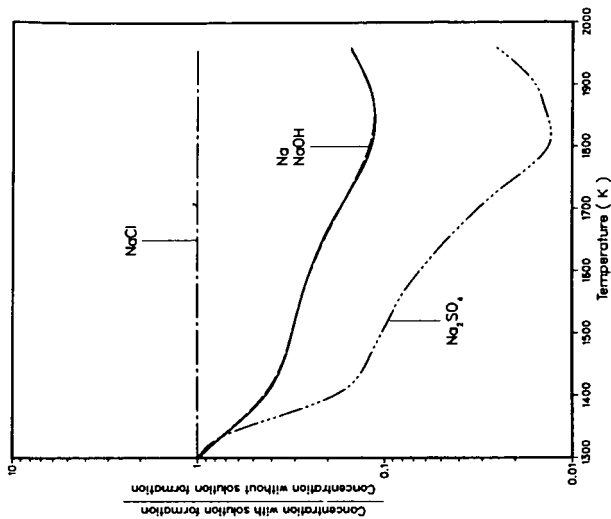
Figure 8. The effect of liquid solution formation between silica and sodium disilicate on the concentrations of species in the gas phase.

Figure 7. The effects of liquid solution formation between silica and sodium disilicate. This figure is to be compared with Figure 1.

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